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(54) Blue glass compositions.

(57) A blue glass composition comprises conventional soda-lime-silica glass ingredients and specific amounts of Fe₂O₃, Co₃O₄, NiO, and optionally Se, resulting in an Illuminant C transmittance of 54% ±3% at one quarter inch thickness, a dominant wavelength of 482nm ±1nm, and a colour purity of 13% ±1%.

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This invention relates generally to blue glass compositions, and more particularly, to blue glass compositions having an Illuminant C transmittance of 54% \pm 3%, a dominant wavelength of 482nm \pm 1nm, and a colour purity of 13% \pm 1%, at a glass thickness of one quarter inch.

Glass compositions having various colours are used, for example, by architects in glazing buildings.

5 Normally, the colour selected by the architect serves several functions. A first function of the colour is to make the glass aesthetically pleasing when viewed from the exterior of the building. Aesthetics will determine the acceptability of a desired particular glass colour and, in part, the desired intensity of the colour. A second function is to reduce the amount of heat absorbed from the exterior of the building to the interior of the building, so that the air conditioning load in the building is reduced. Generally, more colour
10 added to glass results in greater heat absorption. In addition, while colour may readily be added to glass to serve these functions, that glass when coloured still must have an appropriate visible light transmittance value.

Those skilled in the art of formulating glass compositions are familiar with various suitable glass colourants. Thus, a small amount of cobalt oxide is known to produce a cold blue colour widely considered
15 unattractive and undesirable for architectural and certain other uses. A high concentration of nickel is known to produce black glass. Selenium can produce pink or red, and ferrous oxide can produce green glass and contribute to advantageous solar load control properties. The glass colour produced by a mixture of colourants will vary with both the amount and relative proportions used. As noted above, varying the choice and amount of colourants also affects the light transmittance value of the glass. As discussed further below,
20 however, the effect on glass colour and transmittance of mixing multiple colourants and/or varying the amount or relative proportions of the colourants is not reliably predictable.

In the following discussion, certain terms well known to those skilled of the art are used to describe colour in glass. One method of specifying colour is by the use of dominant wavelength and colour purity. These are derived from tristimulus coefficients that have been defined by the CIE (Commission Internationale de l'Eclairage). Numerical values for a given glass colour can be determined by calculating the
25 trichromatic values X, Y, and Z. From the tristimulus values for that glass colour, trichromatic coefficients x, y, and z are then calculated and plotted on a chromaticity diagram. The 1931 Standard Observer response diagram defines the amount of each of three primary colours (x is amber, y is green, and z is blue) required to produce energy of each wavelength from 3,800 Angstroms to 7,500 Angstroms, wherein the green curve
30 is the standard luminosity curve for the human eye. The dominant wavelength and colour purity is then numerically determined with respect to the co-ordinates of Illuminant C, an established light source.

Thus, a glass colour may be specified either by its trichromatic coefficients x and y or by its dominant wavelength and purity values. The lower the colour purity, the closer the colour is to the Illuminant C standard and the closer it is to being a neutral colour.

35 An understanding of the foregoing terms and definitions thereof may be had by referring to the Handbook of Colourimetry prepared by the staff of the Colour Measurement Laboratory, Massachusetts Institute of Technology. This book was printed in 1936 by the Technology Press, Massachusetts Institute of Technology, Cambridge, Mass. Also, a good explanation and list of definitions is given in Colour in Business, Science and Industry, (3 Ed.) John Wiley & Sons (especially pages 170-172, 377-378). Useful
40 also is An Introduction to Colour, John Wiley & Sons (especially pages 105-106).

Those skilled in the art know that adding or substituting one colourant for another and/or changing the amount or relative proportion of colourants in a glass composition affects not only the colour of the glass, i.e., its dominant wavelength and its colour purity, but also affects the light transmittance of the glass and its structural qualities. Furthermore, there is in many cases substantial complexity and unpredictability in these
45 effects. Thus, for example, even if the proper alteration in the composition of a particular colour glass were determined for achieving a desired colour shift, the same alteration, unfortunately, would also alter (for example, unacceptably reduce) the light transmittance of the glass. It may, of course, also undesirably alter the colour purity of the glass. In short, all these factors--dominant wavelength, purity, and light transmittance--are variable, and may vary unpredictably with each other. Developing a new glass composition,
50 therefore, having a particular colour and appropriate light transmittance value, is in some cases like searching for a needle in a haystack. An experimental change in the amount or relative proportion of one or more colourants in a glass composition intended to bring one of these numerical values closer to a target value causes one or both of the other values simultaneously to drift off target (or further off target).

The difficulty of this task, finding the correct glass composition for a coloured glass having the desired
55 dominant wavelength, colour purity, and light transmittance, is discussed in U. S. Patent No. 3,296,004 to Duncan, wherein a neutral brown heat absorbing glass is disclosed. Duncan expressly noted that the development of the particular colour requires a careful consideration of the transmittance characteristics of the glass and that the amounts of the colourants must be carefully controlled to achieve the desired colour

(dominant wavelength and colour purity), transmittance, and heat-absorbing characteristic. Thus, for example, Duncan pointed out that if his glass contained more cobalt oxide than he specified, the colour would be more blue than desired. Considering the glass composition of the present invention for a moment, however, the great unpredictability of this area is well demonstrated by the fact that it employs cobalt oxide in an amount well within the range used by Duncan, yet achieves a blue, not a brown colour. That is, the amount of cobalt oxide used by Duncan to produce brown surprisingly yields the attractive blue colour in combination with the other components of the glass composition of the present invention, notwithstanding the fact that such other components are not normally associated with producing blue coloration.

This inherent unpredictability in achieving specific purity, dominant wavelength, and light transmittance values simultaneously in a glass composition had to be overcome in discovering the glass composition of the present invention. A series of blue glass compositions was fabricated for aesthetic evaluation for automotive and architectural uses, and the like. From amongst the many samples, one was chosen having a very attractive blue colour--the colour of the glass composition of the present invention. In particular, it was a blue having a dominant wavelength of $482\text{nm} \pm 1\text{nm}$ and a purity of $13\% \pm 1\%$. These values correspond to the colour co-ordinates of the glass, i.e., trichromatic coefficients, of about $x = 0.2799$ and $y = 0.2947$.

The task then was to develop a blue glass composition including appropriate colourants which yielded the same dominant wavelength and colour purity, but with a desired Illuminant C transmittance value of $54\% \pm 3\%$. As explained above, however, altering the various colourants, the amounts, and relative proportions in which they were used, for purposes of achieving the correct light transmittance value simultaneously caused the colour, that is the dominant wavelength and purity, to drift off target.

The visible light transmittance value of the blue glass of the present invention is dictated by an important commercial consideration. Specifically, glass of the same composition has to be suitable for both motor vehicle glazing and architectural glazing applications. That is, in order to achieve significant manufacturing cost savings, glass for both architectural glazing and automotive glazing applications had to be producible together on the same float glass production line. To use the same glass in both of these applications, it must have an Illuminant A transmittance at least high enough to meet applicable government standards for motor vehicle glazings, and yet low enough to provide heat load reduction to meet architectural glazing specifications. Thus, an Illuminant C transmittance value of $54\% \pm 3\%$ was determined for the glass, at one quarter inch thickness. This meets various applicable architectural standards and, when used as one of the 0.090 inch thick glass panels (the other 0.090 inch thick glass panel being clear) in a laminated safety glass windshield, yields the desired blue of the invention with an Illuminant A visible light transmittance of at least 70% to meet current U.S. government standards for motor vehicle windshields.

Dozens of experimental glass compositions were tried without success. The numerous variables affecting colour in a glass composition, e.g., selection of colourant(s), their amounts, relative amounts, etc., and the unpredictability of the type or degree of change effected by varying one or more of them led to failure after failure. The search continued and dozens of additional experimental glass compositions were tried. Those skilled in the practical aspects of this art will understand the very considerable effort and expense involved in a research and development program of this nature. Still the glass compositions which provided the necessary light transmittance together with the selected dominant wavelength and the selected purity were undiscovered. More time, money, and effort were expended to produce and test dozens of additional experimental glass compositions. All of these were also unsuccessful.

Finally a glass composition was produced and tested and found to have the needed Illuminant C transmittance of $54\% \pm 3\%$ in conjunction with the desired blue colour having a dominant wavelength equal to $482\text{nm} \pm 1\text{nm}$ and a colour purity equal to $13\% \pm 1\%$. Furthermore, as disclosed below, this was achieved using four colourants, each readily commercially available at reasonable cost and each used in a practical, easily measured quantity.

A blue glass having approximately the same transmittance, dominant wavelength, and excitation purity values, but containing only three colourants, is disclosed in U.S. Patent No. 4,866,010 to Boulos et al. However, the patent does not suggest that a fourth colourant may be added, and the proportions of the original three colourants modified, to achieve virtually the same values for transmittance, dominant wavelength, and colour purity as for the present inventive glass composition. Specifically, the patent does not suggest, and in fact teaches away from, the use of nickel, which typically imparts a reddish-brown colour to glass, as a component of the present inventive blue glass composition.

U.S. Patent No. 2,938,808, subsequently reissued as U.S. Patent No. Re 25,312, discloses as a new article of manufacture a neutral colour sheet of glass having a thickness in the range of $1/8$ - $1/4$ inch. The glass is suitable for glazing purposes and has a substantially uniform transmittance for light in the portion of the spectrum between 440 and 660 millimicrons, a colour purity below 7%, a total solar energy transmittance between 40% and 48%, and a total luminous transmittance between 35% and 45%, at a thickness of

1/4 inch. The disclosed glass composition consists essentially of base ingredients in percentages by weight as follows: 60-75% SiO₂, 11-20% Na₂O, 0-10% K₂O, the sum of the Na₂O and the K₂O being 11-21%, 6-16% CaO, and 0-10% MgO, the sum of the CaO and MgO being 6-18%, together with 0.4% Fe₂O₃, 0.0076-0.008% Co₃O₄, 0.009-0.126% NiO, and 0.005-0.0056% Se. The patent teaches that the amounts of the colourants Fe₂O₃, Co₃O₄, NiO, and Se are greater when the thickness of the sheet is less than 1/4 inch, and is approximately twice the above listed amounts for each colourant when the thickness of the sheet is 1/8 inch.

U.S. Patent No. 3,723,142 discloses a neutral gray coloured heat absorbing glass having a low colour purity. The glass is defined as consisting essentially of the following base components in percentages by weight: 68-75% SiO₂, 0-5% Al₂O₃, 5-15% CaO, 0-10% MgO, the sum of the CaO and the MgO being 6-15%, 10-18% Na₂O, and 0-5% K₂O, the sum of the Na₂O and the K₂O being 10-20%, together with colouring components of 0.1-0.5% Fe₂O₃, 0.003-0.02% Co₃O₄, 0.0005-0.001% Se, and negligible NiO. The patent states that the quantity of NiO should be less than about 0.002% and preferably less than 0.0004%.

U.S. Patent No. 3,498,806 discloses various specific compositions for glasses of "generally blue" coloration, along with compositions for clear glass and glasses of green or other colouring. None of these compositions, however, is the same or even similar to the composition of the glass of the present invention. They differ most notably in both the selection of colourants (using certain colourants not used in the present invention and others which are used) and the amounts and relative proportions of the colourants. Specifically, the patent does not disclose the use of nickel in the glass composition.

Finally, U.S. Patent No. 4,101,705 discloses neutral bronze glazings having a dominant wavelength in the range of 570nm to 580nm and a colour purity from 2% to 6% the weight percentages of Co₃O₄ and NiO are lower, and the weight percentage of Se is higher, than the allowable ranges for these colourants in the present invention.

It must be noted that the prior art referred to hereinabove has been collected and examined only in light of the present invention as a guide. It is not to be inferred that such diverse art would otherwise be assembled absent the motivation provided by the present invention, nor that the cited prior art when considered in combination suggests the present invention absent the teachings herein.

Accordant with the present invention, a blue glass composition having an Illuminant C transmittance of 54% ±3% at a glass thickness of one quarter inch, a dominant wavelength of 482nm ±1nm, and a colour purity of 13% ±1%, has surprisingly been discovered. The glass consists essentially of 68% to 75% by weight SiO₂; up to 5% by weight Al₂O₃; 5% to 15% by weight CaO; up to 10% by weight MgO, wherein CaO + MgO is 6% to 15% by weight; 10% to 18% by weight Na₂O; up to 5% by weight K₂O, wherein Na₂O + K₂O is 10% to 20% by weight; 0.189% to 0.478% by weight Fe₂O₃; 0.0048% to 0.0080% by weight Co₃O₄; and additional colourant selected from the group consisting of: a mixture of 0.00005% to 0.0153% by weight NiO and 0.00005% to 0.0003% by weight Se; and 0.0048% to 0.0153% by weight NiO.

The present invention also includes a method for colouring a basic soda-lime-silica glass batch to produce precise colour and transmittance properties by admixing into the batch specific quantities of Fe₂O₃, Co₃O₄, NiO, and optionally Se.

The glass compositions of the present invention are particularly suited for the manufacture of blue-coloured automotive and architectural glazings.

The glass of the present invention generally comprises a basic soda-lime-silica glass composition having specific colourants in specific quantities therein.

The basic soda-lime-silica glass comprises 68% to 75% by weight SiO₂, up to 5% by weight Al₂O₃, 5% to 15% by weight CaO, up to 10% by weight MgO, with the proviso that CaO + MgO is 6% to 15% by weight of the glass, 10% to 18% by weight Na₂O, and up to 5% by weight K₂O, with the proviso that Na₂O + K₂O is 10% to 20% by weight of the glass. Silica forms the glass matrix. Alumina regulates the viscosity of the glass, and prevents devitrification. Calcium oxide, magnesium oxide, sodium oxide, and potassium oxide act as fluxes to reduce the melting temperature of the glass. Furthermore, the alumina, calcium oxide, and magnesium oxide act together to improve the durability of the glass.

Colourants are admixed into the molten batch of basic soda-lime-silica glass (which is otherwise clear), according to the present invention, to impart a blue colour and achieve specific transmittance and chromatic characteristics. By "admixing into the molten batch" is also contemplated the addition of the colourants along with the basic glass batch ingredients simultaneously into the melting tank. Ferric oxide (Fe₂O₃) is present in an amount from 0.189% to 0.478% by weight of the glass. Additionally, cobalto-cobaltic oxide (Co₃O₄) is present in an amount from 0.0048% to 0.0080% by weight of the glass. Finally, nickel oxide (NiO) is present, either alone or in combination with selenium (Se), as follows: 0.0048% to 0.0153% by weight NiO; or a mixture of 0.00005% to 0.0153% by weight NiO and 0.00005% to 0.0003% by weight Se.

Glass compositions according to the present invention are blue in reflection and transmission and have

an Illuminant C transmittance of 54% \pm 3% at a glass thickness of one quarter inch, a dominant wavelength of 482nm \pm 1nm, and a colour purity of 13% \pm 1%. The tristimulus coefficients are approximately $x = 0.2799$ and $y = 0.2947$.

5 Examples 1 & 2

Various quantities of sand, soda ash, dolomite, limestone, salt cake, sodium nitrate, rouge, cobalto-cobaltic oxide, and selenium metal and/or nickel oxide are combined as set forth in Table I.

10 Table I

Glass Batch Ingredients (Grams)		
Ingredient	Example 1	Example 2
Sand	1000.0	1000.0
Soda Ash	311.1	311.3
Dolomite	260.8	261.2
Limestone	70.4	70.1
Salt Cake	10.9	11.0
Sodium Nitrate	10.4	10.4
Rouge	3.430	5.301
Co ₃ O ₄	0.1107	0.1118
NiO	0.1345	0.0660
Selenium Metal	0.0	0.0147

The aforementioned glass batch ingredients are melted together to form glass compositions as set forth in Table II.

30 Table II

Glass Compositions (wt%)		
Component	Example 1	Example 2
SiO ₂	73.93	72.62
Na ₂ O	12.63	13.70
CaO	8.56	8.67
MgO	4.10	4.09
Al ₂ O ₃	0.12	0.11
SO ₃	0.28	0.30
TiO ₂	0.01	0.01
K ₂ O	0.06	0.04
Fe ₂ O ₃	0.290	0.430
Co ₃ O ₄	0.0055	0.0054
NiO	0.0072	0.0035
Se Metal	0.0	0.00015

The properties of the resultant glass compositions, at a thickness of 1/4 inch, are set forth in Table III.

Table III

Optical Properties (at 1/4 inch)		
	Example 1	Example 2
Illuminant C Transmittance	53.4%	51.4%
Dominant Wavelength	481.4nm	481.5nm
Colour Purity	13.9%	13.9%

These examples may be repeated with similar success by substituting the generically or specifically described reactants and/or reactant conditions recited herein for those actually used in the preceding example.

Claims

1. A blue-coloured glass having an Illuminant C transmittance of 54% \pm 3% at a glass thickness of .63cm (one quarter inch), a dominant wavelength of 482nm \pm 1nm, and a colour purity of 13% \pm 1%, the glass including:

- A. 68% to 75% by weight SiO₂;
- B. up to 5% by weight Al₂O₃;
- C. 5% to 15% by weight CaO;
- D. up to 10% by weight MgO, wherein CaO + MgO is 6% to 15% by weight;
- E. 10% to 18% by weight Na₂O;
- F. up to 5% by weight K₂O, wherein Na₂O + K₂O is 10% to 20% by weight;
- G. 0.189% to 0.478% by weight Fe₂O₃;
- H. 0.0048% to 0.0080% by weight Co₃O₄;

and

- I. additional colourant selected from the group consisting of:

- i. a mixture of 0.00005% to 0.0153% by weight NiO and 0.00005% to 0.0003% by weight Se; and
- ii. 0.0048% to 0.0153% by weight NiO.

2. A glazing for automotive or architectural use prepared from the blue-coloured glass of Claim 1.

3. A method for colouring a basic soda-lime-silica glass, to prepared blue-coloured glass having an Illuminant C transmittance of 54% \pm 3% at a glass thickness of .63cm (one-quarter inch), a dominant wavelength of 482nm \pm 1nm, and a colour purity of 13% \pm 1%, the method comprising admixing to a molten batch of basic soda-lime-silica glass, colourants, including:

- A. 0.189% to 0.478% by weight Fe₂O₃;
- B. 0.0048% to 0.0080% by weight Co₃O₄; and
- C. additional colourant selected from the group consisting of:
 - i. a mixture of 0.00005% to 0.0153% by weight NiO and 0.00005% to 0.0003% by weight Se; and
 - ii. 0.0048% to 0.0153% by weight NiO.

4. A method for preparing a blue-coloured glass having an Illuminant C transmittance of 54% \pm 3% at a glass thickness of .63cm (one quarter inch), a dominant wavelength of 482nm \pm 1nm, and a colour purity of 13% \pm 1%, the method including admixing and melting together sand, soda ash, dolomite, limestone, salt cake, sodium nitrate, rouge, cobalto-cobaltic oxide, selenium, and optionally nickel oxide, in quantities sufficient to form the glass of Claim 1.